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Direct detection of Calcium Carbonate Scaling via a Pre-Calcified Sensitive Area of a Quartz Crystal Microbalance

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Abstract

In an industrial cooling circuit supplied with raw river water, the scaling phenomenon can reduce cooling efficiency and even lead to the shut down of the power plant. During the last twenty years, various methods have been developed in order to estimate the scaling propensity of natural waters, which involve the precipitation of calcium carbonate (CaCO₃), the main component of scale. The FCP (Fast Controlled Precipitation) is a non-

electrochemical method which consists in CO₂ degassing from water by a moderate stirring. FCP allows quantifying the scaling propensity for natural water. However, FCP is not well adapted in the case of waters with low scaling propensities, or for *in situ* measurements.

In this study, a quartz crystal microbalance with a pre-calcified sensitive electrode or SQCM (Scaling Quartz Crystal Microbalance) was developed. The sensitive surface of this gravimetric sensor could be used as an adsorption layer for calcium carbonate nuclei present in water. Thus, SQCM method is able to detect the phenomenon of scaling, even if the water does not precipitate, due to its high gravimetric sensitivity. This method is described in details in this paper, and was successfully applied to evaluate the scaling propensity of synthetic waters. SQCM could be used *in situ* to assess the efficiency of humic substances in synthetic water towards scaling.

Keywords: Scaling, calcium carbonate, quartz crystal microbalance, pre-calcified sensitive surface, saturation level, humic substances.

Abbreviations:

δ : Saturation Level.

δ_{limit} : Limiting Saturation Level.

EQCM: electrochemical quartz crystal microbalance

GTT: Gravimetric Test on Tubes

QCM: Quartz Crystal Microbalance

SCE: Saturated Calomel Electrode

SQCM: Quartz Crystal microbalance with pre-calcified surface of the electrode

TOC: Total Organic Carbon

TSS: Total Suspended Solid

1. Introduction

Scaling is a major concern in different industrial processes and domestic installations [1,2]. Undesirable scale deposits often cause numerous technical problems, such as total or partial obstruction of pipes, leading to a decrease in flow rate, reduced heat transfer, seizure of valves and clogging of filters. The non-productive expenses related to scaling were estimated at 1.5 billion euros per year in France [3]. In nuclear power plants, the scaling phenomena can reduce efficiency and limit the power production. Therefore, they are important needs to develop some appropriate methods to follow this phenomenon in order to better prevent it.

During the last twenty years, various methods have been developed in order to estimate the scaling propensity of natural waters [4]. These methods involve the precipitation of calcium carbonate (CaCO_3), the main component of scale. These methods can be roughly divided into two categories: electrochemical methods and non-electrochemical methods. Among the first ones, the electrochemical quartz crystal microbalance or EQCM has been used for twenty years to promote accelerated scaling by imposing an electrochemical potential on its surface [5]. This technique allows *in situ*, fast (about an hour) and sensitive (nanograms of generated calcium carbonate) measurements of the scaling phenomenon. A decisive improvement was made by perfectly controlling the hydrodynamics with a submerged jet device incorporating a quartz crystal microbalance [6]. However, in the EQCM method, the scaling phenomenon is greatly accelerated by an electrochemical reaction on the electrode surface. Thus, the resulting scaling is not really representative of the natural phenomenon in an industrial circuit. It has been shown that, in the electrochemical method, the water samples reaches very high saturation levels in the vicinity of the electrode [7]. In this case, the water is highly instable and is characterised by the spontaneous precipitation of CaCO_3 . The thermodynamic conditions are no longer the same as in a real scaling phenomenon.

Among the non-electrochemical methods, the Fast Controlled Precipitation (FCP) method was developed by taking into consideration its representativeness relative to a real scaling phenomenon. It consists in degassing of CO_2 from the test water by a moderated agitation leading to a slight supersaturation regarding CaCO_3 , in order to evaluate the scaling potential of waters. Still the FCP is a laboratory method which cannot be easily applied in the industrial field. Thus, the Gravimetric Test on Tubes (GTT) has been developed [8]. In this method, tubes of various types were previously encrusted by a pre-scaling step so that the influence of tubes nature towards scaling could be eliminated. Moreover, the newly formed surface of CaCO_3 is active for the adsorption of CaCO_3 formed at a later stage. GTT has been applied for evaluating the scaling potential of the water in a cooling circuit of a power plant. The results showed that, even with a double treatment by H_2SO_4 and by a scale inhibitor, water in a cooling circuit still kept a scaling potential of $0,3\text{g/m}^2/\text{day}$. However, GTT suffers from the slow measurement due to the “out-situ” weighing by a classic balance.

This prompted us to develop a quartz crystal microbalance with a pre-calcified sensitive surface, or SQCM. The choice of quartz crystal microbalance was fully justified. Indeed, it enables to continuously follow extremely tiny CaCO_3 mass changes. The electrochemical pre-calcification step of the electrode surface is well controlled. It can also eliminate the influence of support materials nature towards scaling [8].

In this paper, the SQCM method is described in details and is applied to evaluate the scaling propensity of synthetic waters. Additionally, SQCM tests were carried out in the presence of humic substances, which is often found in natural river waters. These tests gave in order to get some insight into the influence of humic substances on water scaling propensity.

2. Experimental

2.1. Studied waters

The synthetic waters (60, 100, 150 or 200 mg/L in calcium) used in this work were prepared by dissolving solid calcium carbonate (AnalaR NORMAPUR VWR, 99.7% purity) in pure water (Milli.Q water, 18.2 M Ω cm resistivity and TOC <5 mg L⁻¹) by bubbling CO₂ gas. After the solid dissolution, the pH of the solution was about 5.2-5.5. Under those experimental conditions, no spontaneous precipitation of CaCO₃ occurred. The solution was then filtered with a Millipore filter (514-8073 Whatman, 0.45 μ m porosity) to remove any impurities.

A stock solution containing humic substances (5 mg L⁻¹) was obtained by dissolving humic acid as sodium salt (technical grade, Aldrich) in 2L of synthetic water ([Ca²⁺] = 100 mg.L⁻¹). This stock solution was diluted to obtain solutions with lower concentrations of humic substances (0.2, 0.5, 1.0, 2.0 and 5.0 mg L⁻¹). In natural water, the concentration of humic substances is only part of the TOC value. Those values vary widely, depending on the source and the seasons. According to Klimenko *et al.*, TOC values between 0.7 and 17 mg L⁻¹ were obtained for water from various natural environments around the world [9]. This range of humic acid concentration was retained in this work.

Turbidity was measured using a TURB 430IR turbid meter. The turbidity value was evaluated from the average of five consecutive measurements.

To determine the TSS (Total Suspended Solid) concentration, 250mL of solution were filtered through a glass fiber filter (0.7 μ m porosity). The filter was dried in an oven at 105 °C for 1 h and then weighted with a precision balance. The TSS concentration was calculated by dividing the mass obtained by the initial volume of the sample (250 mL). The values of TSS and turbidity are reported in Table S1 (Supplementary Data).

2.2 XRD characterization

XRD measurements were performed on a Panalytical (Empyrean Diffractometer Panalytical) device equipped with a detector Pixcel 1D, a copper anode as the source of radiation ($1.54 \text{ \AA} / K\alpha$), with a power of 45 kV and under an operating temperature of $20 \text{ }^\circ\text{C}$. For samples in the form of powders, the total acquisition time per sample was 31 min, the diffraction angle 2θ was in the range 15 ° - 90 ° , with a resolution of 0.0131 ° . The measurement parameters were the same for samples of calcium carbonate deposited on the QCM electrode. However, a longer acquisition time (19 hours 30 min) was necessary because the amount of material available on the QCM electrode surface was very small (around a few μg).

The different crystalline forms of calcium carbonate were quantified by XRD measurements, as described in the Supplementary Data.

2.3. Pre-calcification of the surface of the electrode in SQCM

The gold electrode (gold deposited on the quartz resonator) involved in SQCM was pre-calcified by using an electrochemical procedure described elsewhere [6]. The deposition conditions in a synthetic water solution ($[\text{Ca}^{2+}] = 100\text{mg L}^{-1}$) were as follows: a temperature of $35 \text{ }^\circ\text{C}$, a flow rate of 300 mL min^{-1} and an applied potential of -1.0 V / SCE . When the electrode surface was totally covered by calcium carbonate (stabilization of the chronoelctrogravimetric curve), the polarization and the solution flow were stopped.

2.4. SQCM set up

The pre-calcified electrode (see above) was installed in a cell that is representative of an industrial fluid stream (studied water) with a laminar flow, as shown in Fig. 1:

((Figure 1))

This set-up simulates pipes for a cooling circuit. The fluid flows parallel to the surface of the walls under a laminar regime (flow rate=300mL min⁻¹) In a typical SQCM experiment, the flow of water is provided by a gear pump which is rotated by an electric motor (GEC Alstom TBN103) slaved to a stabilized power supply. The pumping and the connecting systems ensured a particularly regular and stable flow. In order to perform gravimetric measurements *via* the SQCM, the following devices were used to measure and record the signals describing the microbalance frequency changes, in order to estimate the mass changes: a frequency meter (Fluke universal counter PM6685) and a computer equipped with a lab-made software (FRQM software). This allowed to control the different devices and to record numerically the experimental curves.

One liter of pre-heated water was introduced in a Teflon beaker. Two different ways of operating were used in this study. On the one hand, the water with an initial pH value around 6.0 was continuously stirred for CO₂ degassing. In this configuration, pH and microbalance frequency changes were recorded over time (configuration I). On the other hand, the water with an initial pH value in the range 6.8-7.8 obtained by CO₂ pre-degassing was used in SQCM system. In this case, CO₂ degassing of the solution was blocked both by closing carefully the openings in the beaker lid and stopping the solution stirring. The saturation level, δ , was maintained below the spontaneous precipitation threshold (configuration II).

3. Background for the heterogeneous precipitation and scaling on a pre-calcified surface

In this section, the process of heterogeneous precipitation (scaling) on a pre-calcified surface is discussed [11]. Regarding the last step during this scaling formation, the balance between precipitation and dissolution of scaling can be described by the following equation (1):



where R represents the reactive species such as Ca^{2+} and CO_3^{2-} and P represents the reaction product, *i.e.* calcium carbonate in solid phase. k_+ and k_- are the kinetic rate constants related to the reactions of precipitation or dissolution, respectively. The equilibrium constant K_{eq} , related to the formation of calcium carbonate, is given by equation (2):

$$\frac{k_+}{k_-} = \frac{[P]_{eq}}{[R]_{eq}} = K_{eq} \quad (2)$$

According to Blum [11], the relationship between the reaction rate, V_R , and the free energy, ΔG , can be described by the following equation (3):

$$V_R = \frac{d[CaCO_3]}{dt} = -\frac{S}{V} k [1 - \exp(-\frac{\Delta G_{pre} + \Delta G_{dis}}{R_g T})]^n = -\frac{S}{V} k [1 - \exp(\frac{\Delta G}{R_g T})]^n \quad (3)$$

where V_R is the reaction rate, S is the reaction surface, V is the volume of the solution, ΔG_{pre} and ΔG_{dis} are, respectively, the free energy released in CaCO_3 formation process and the free energy expended in dissolution of calcium carbonate, ΔG is the total free energy of the reaction, k is the constant of the reaction and n the reaction order.

The free energy of the reaction, ΔG , depends on the saturation level, δ , of the solution according to the following equation (4):

$$\Delta G = \frac{R_g T}{2} \ln \delta \quad (4)$$

Equation 3 can be rewritten as:

$$V_R = \begin{cases} k' [\delta^{\frac{1}{2}} - 1]^n & \delta > 1 \\ k'' [1 - \delta^{\frac{1}{2}}]^n & \delta < 1 \end{cases} \quad (5)$$

where k' and k'' can be define as:

$$k' = \frac{S}{V} k \text{ and } k'' = -\frac{S}{V} k \quad (6)$$

When $\delta > 1$, V_R is the scaling rate and when $\delta < 1$, V_R is the dissolution rate. This approach will be used in the following to explain the shape of the SQCM results during the scaling process before the threshold of homogeous precipitation.

4. Results and discussion

4.1. Comparison of QCM and SQCM methods towards scaling

A comparison between two scaling tests, the first one involving SQCM with a pre-calcified surface and the second one involving a “classical” QCM with a bare gold surface electrode has been carried out by using configuration I (see paragraph 2.4). For each test, the same synthetic water (pH = 6) was stirred in order to accelerate the degassing of CO₂, which increases the pH of the solution [13]. The evolution of the mass of calcium carbonate deposited on the SQCM and the QCM are presented in Figure 2:

((Figure 2))

Before the homogeneous precipitation threshold is reached (dashed line in Fig.2.), the mass of calcium carbonate deposited on the QCM electrode with a bare gold surface does not evaluate. At the same time, a significant change in the mass of calcium carbonate deposited on SQCM is observed. This change is related to change in pH and, therefore, to the saturation level of the solution. At the beginning, the solution is aggressive ($\text{pH} = 6$) and leads to the dissolution of the pre-calcified layer. Therefore, a mass reduction is initially detected. When the pH increases, the solution becomes increasingly calcifying and the scaling rate gradually increases. When the solution exceeds the calco-carbonic equilibrium ($\delta > 1$), the scaling rate becomes more important than that of dissolution. Thus, the scale mass detected by SQCM starts to increase.

A water is considered to be metastable when its saturation level, δ , is between 1 and the homogeneous precipitation threshold [13]. Recent SAXS studies showed the presence of calcium carbonate nuclei in a metastable water before homogeneous precipitation [14,15,16]. In the case of the SQCM method, the local calco-carbonic equilibrium is broken near the scale surface of the pre-calcified layer, where the saturation level is higher than in the bulk solution. Thus, the calcium carbonate layer acts as adsorption sites for the calcium carbonate nuclei present in water. The related change in mass can be monitored very finely (at nanograms). In conclusion, the SQCM method is able to detect the scaling phenomenon even if the water does not precipitate, and is much more sensitive than a classical QCM with a bare gold surface.

After the homogeneous precipitation threshold (dashed line in Fig.2.), both QCM and SQCM methods detect an increase of the mass of calcium carbonate and/or a strong change of the solution properties. This is due to large particles of calcium carbonate which appear after the precipitation.

4.2. Relationship between instantaneous scaling rate, V_E^{inst} , and saturation level, δ

Experiments were then performed under different δ values according to configuration II (see paragraph 2.4) in order to correlate the scaling rate and the saturation level of the studied waters. Figure 3 shows some $m(t) - t$ curves obtained by SQCM for different synthetic waters:

((Figure 3))

During a typical SQCM experiment, the CO_2 degassing of water is prevented. This maintains a constant saturation level, δ , throughout the test. Fig.3 shows that the higher δ , the faster the increase in mass over time. For a solution having a low sursaturation level ($[\text{Ca}^{2+}] = 60 \text{ mgL}^{-1}$), the dissolution rate of the calcium carbonate layer is faster than its growth rate. Thus, the overall mass of the pre-calcified surface decreases, which gives a negative scaling rate. It must be noticed that water is aggressive during most of the test (δ in the range 0.8-1.1). However, even if the system water flow is almost in closed circuit, a small CO_2 outgassing happens during the experiment. This is responsible for a very slow increase in pH (about 0.1 units per hour). For each point of a given $m(t) - t$ curve, the saturation level, δ , can be calculated with the Legrand-Poirier method [17]. The instantaneous scaling rate, V_E^{inst} , can be calculated according to the following equation (7):

$$V_E^{inst} = \frac{dm(t)}{dt} \quad (7)$$

where $m(t)$ corresponds to the mass of calcium carbonate detected at the time t by the SQCM electrode.

Figure 4 shows the evolution of the instantaneous scaling rate, V_E^{inst} , over $(\delta^{\frac{1}{2}} - 1)$ obtained from several SQCM tests performed in synthetic waters with different saturation levels:

((Figure 4))

Several experiments, involving different calcium concentrations, were used in order to explore a large range of saturation levels. These series of experimental results allow a tendency between the saturation level and the scaling speed to be given: two different coefficients are applied in order to distinguish the scaling process (when the saturation level >1) and the re-dissolution process (when the saturation level <1). A fitting of the experimental data was carried out, based on Equation (5) which establishes a relationship between V_E^{inst} and $(\delta^{1/2}-1)$. The following equations were obtained (8):

$$V_E^{inst} = \begin{cases} 0,105[\delta^{\frac{1}{2}} - 1]^{2,46} & \delta > 1 \\ -0,193[1 - \delta^{\frac{1}{2}}]^{1,55} & \delta < 1 \end{cases} \quad (8)$$

As explained before (§ 3), when $\delta > 1$, the instantaneous scaling rate, V_E^{inst} , is positive which indicates a scale mass gain. When $\delta < 1$, the instantaneous scaling rate, V_E^{inst} , is negative which indicates a scale mass loss. The reaction order values are non-integer, which suggests of complex kinetic mechanisms.

4.3. Influence of humic substances monitored by SQCM

Synthetic waters in the presence of humic substances were tested by SQCM (configuration II), as shown in Figure 5:

((Figure 5))

Figure 5 shows that SQCM is very sensitive and able to detect the inhibitor effect of humic substances on scaling [13, 18]. The inhibitor efficiency of humic substances measured by the SQCM method can be evaluated by using Equation 9:

$$\psi_{E-QCM-E} = \frac{V_{E0}^{ave} - V_{Ei}^{ave}}{V_{E0}^{ave}} \times 100\% \quad (9)$$

where V_{E0}^{ave} is the average scaling rate for water in the absence of humic substances and V_{Ei}^{ave} is the average scaling rate of the same water in the presence of humic substances. The inhibitor efficiencies for different concentrations of humic substances are reported in Table 1:

((Table 1))

The average scaling rate decreases when the humic substance concentration increases. An optimal inhibitor effect was obtained for a humic substances concentration of 2 mg L⁻¹. This result is in good agreement with the results previously obtained with humic substances [13].

In addition, XRD was performed on the CaCO₃ layer formed by SQCM after 4h in a synthetic water, in the presence of humic substances (Fig. 6):

((Figure 6))

In Fig.6, the peaks used for the quantification of the different crystalline forms are identified by letters of green color. The peak intensities and the related molar ratios were calculated for each crystalline form and are presented in Table 2:

((Table 2))

Table 2 shows that the proportions of the different forms of calcium carbonate are largely modified in the presence of humic substances. 4h after scaling, the proportion of calcite is higher in the presence of humic substances, compared to that obtained in the absence of humic substances. In conclusion, the presence of humic substances promotes the formation of calcite, the most thermodynamically stable crystalline form of calcium carbonate.

5. Conclusions

A novel method, namely the SQCM method, has been developed to assess the scaling propensity for a given water. This method involves a pre-calcified surface formed by an electrochemical procedure. Comparing to classic electrochemical QCM method, the SQCM method shows a better sensitivity, especially for water in the presence of inhibitors, such as humic substances. This may be due to the fact that during an SQCM test, the scaling phenomenon is much slower, and therefore closer to the real scaling phenomenon. Comparing to FCP and GTT methods, SQCM shows some potential for in-situ measurement in an industrial environment. In addition, a relationship was found between the scaling rate V_E measured by this method and the water saturation level, which make it possible to quantify the scaling potential of a tested water.

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Fig. 1. Scheme of the SQCM set-up [10].

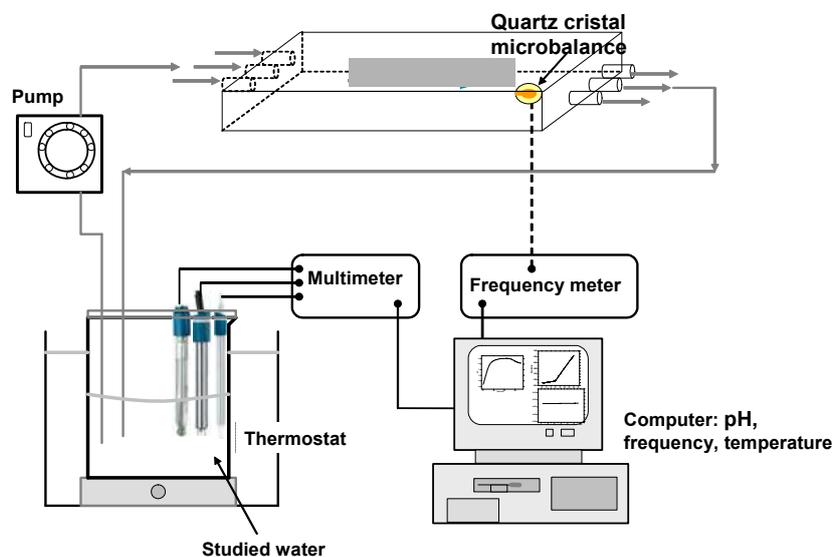


Fig.2. Evolutions of the pH of the solution (synthetic water with $[Ca^{2+}] = 100\text{mg L}^{-1}$) and the mass of calcium carbonate deposited on the QCM surface ($T = 30^\circ\text{C}$). Blue line : SQCM (with pre-calcified surface) and red line: QCM with bare gold electrode.

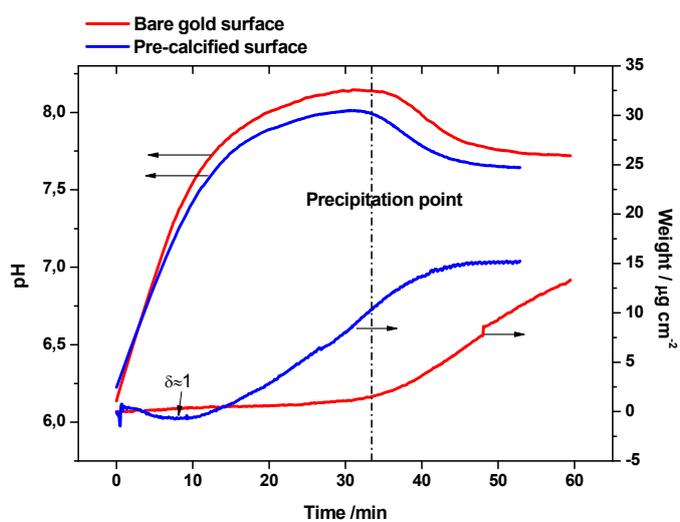


Fig.3. Calcium carbonate mass evolution over time through SQCM measurements ($T = 35\text{ }^{\circ}\text{C}$, $\text{pH} = 7.1\text{-}7.4$, flow rate = 300 mL min^{-1}) for four synthetic water concentrations ($[\text{Ca}^{2+}] = 60\text{ mg L}^{-1}$, $[\text{Ca}^{2+}] = 100\text{ mg L}^{-1}$, $[\text{Ca}^{2+}] = 150\text{ mg L}^{-1}$ and $[\text{Ca}^{2+}] = 200\text{ mg L}^{-1}$).

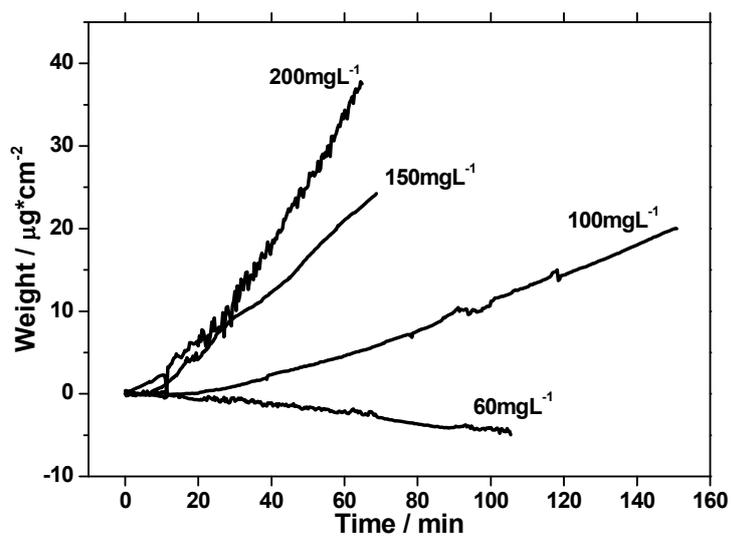


Fig.4. Evolution of the instantaneous scaling rate, V_E^{inst} , over $(\delta^{1/2}-1)$ variable. The experimental points were obtained by using several SQCM tests ($T = 35^\circ \text{C}$, flow rate = 300 mL min^{-1}) with different synthetic water concentrations, $[\text{Ca}^{2+}] = 60 \text{ mg L}^{-1}$, 100 mg L^{-1} , 150 mg L^{-1} , 200 mg L^{-1} and pH in the range 6.8-7.8. The red line corresponds to the fit of the experimental data with the model developed in §3.

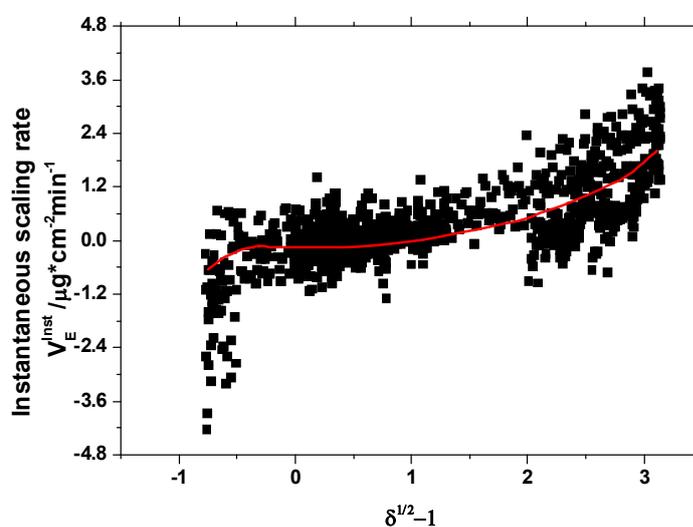


Fig.5. Changes of the calcium carbonate mass over the time through SQCM measurements (flow rate = 300 mL min^{-1} , temperature = $35\text{ }^{\circ}\text{C}$) for a synthetic water ($[\text{Ca}^{2+}] = 100\text{ mg L}^{-1}$, $\text{pH} = 7.2\text{-}7.3$) in presence of humic substances at different concentrations (0 mg L^{-1} , 0.2 mg L^{-1} , 0.5 mg L^{-1} , 1 mg L^{-1} , 2 mg L^{-1} , 5 mg L^{-1}).

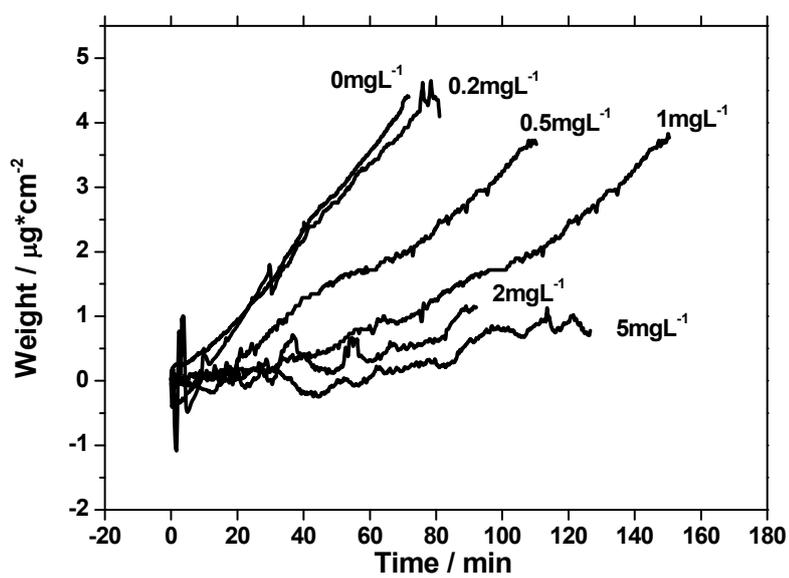
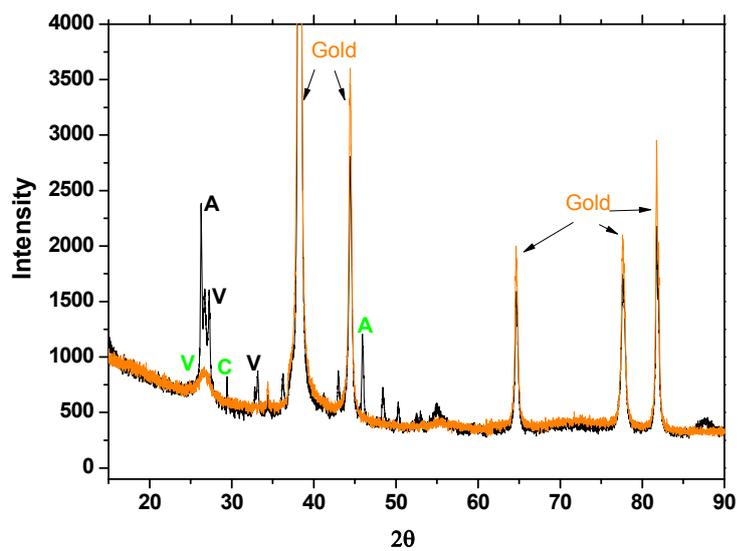
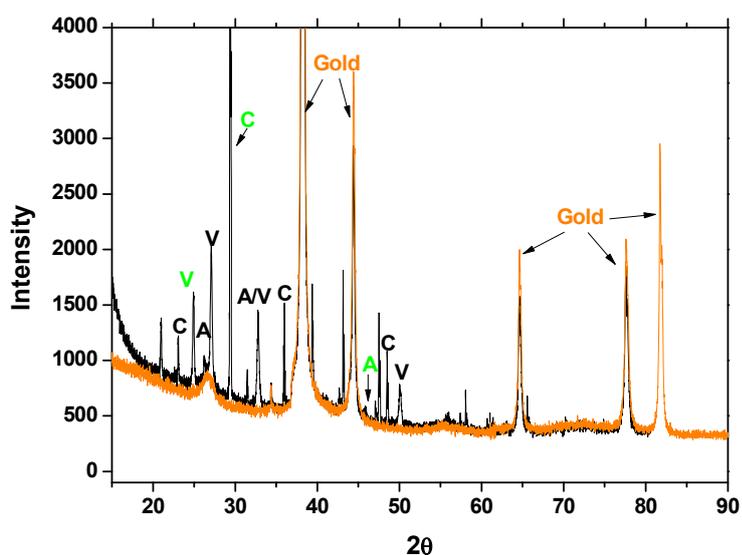


Fig. 6. XRD spectrum obtained for the pre-calcified surface after 4h in synthetic water (pH = 7.2-7.4, $[Ca^{2+}] = 100 \text{ mg L}^{-1}$) through SQCM test (flow rate = 300 mL min^{-1} , temperature = 35°C): (a) pure synthetic water without humic substances (b) with the presence of humic substances (concentration : 5 mg L^{-1}). A = aragonite, C = Calcite, V = Vaterite.



(a)



(b)

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Table 1. Average scaling rates, V_E^{ave} , obtained through SQCM measurements (flow rate = 300mL min⁻¹, temperature = 35 ° C) for a synthetic water (pH = 7.2-7.3, [Ca²⁺] = 100mg L⁻¹) in the presence of humic substances (0 mg L⁻¹, 0.2 mg L⁻¹, 0.5 mg L⁻¹, 1mg L⁻¹, 2mg L⁻¹).

Concentration in humic substance mg L ⁻¹	[Ca ²⁺] Mol L ⁻¹	V_E^{ave} $\mu\text{g cm}^{-2} \text{min}^{-1}$	Inhibitor efficiency (SQCM) %
0	0.0025	7.44	0
0.2	0.0025	5.93	20.3
0.5	0.0025	3.39	54.4
1	0.0025	2.14	71.3
2	0.0025	0.97	86.9
5	0.0026	0.85	88.6

Table 2. Calculated molar ratios for different morphologies of CaCO₃ on the SQCM electrode (C = Calcite, V = Vaterite and A = Aragonite): after 4 h, after 4h in the presence of humic substances (5 mg L⁻¹). All experiments were performed in synthetic water ([Ca²⁺] = 100 mg L⁻¹).

	Water	Water + humic substances
C%	7.9	42
A%	36	7.4
V%	56	50

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> A quartz crystal microbalance with a pre-calcified sensitive electrode was developed. > The sensitive surface of this gravimetric sensor can be used as an adsorption layer for calcium carbonate nuclei present in water. > It was successfully applied to evaluate the scaling propensity of synthetic waters. > This sensor can be used *in situ* to assess the efficiency of humic substances in synthetic water towards scaling.

Supplementary Data – Manuscript DES-D-14-00440**Direct detection of Calcium Carbonate Scaling via a Pre-Calcified Sensitive Area of a Quartz Crystal Microbalance**

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Table S1. Values of TSS and turbidity of the prepared solutions containing humic acid.

[Ca ²⁺] (mgL ⁻¹)	Humic substances (mgL ⁻¹)	Turbidity (NTU)	TSS (mgL ⁻¹)
100	0	0	-
100	0.2	0.11	-
100	0.5	0.32	-
100	1	0.54	-
100	2	0.93	-
100	5	-	-

1) Quantification of the different crystalline forms of calcium carbonate by XRD measurements

XRD measurement can qualify and quantify the different crystalline forms of calcium carbonate. The diffraction peaks are associated with atomic planes of the sample, and the estimated Miller indices are used for identifying different crystalline forms present in the sample of calcium carbonate. Three crystalline forms, calcite, aragonite and vaterite were identified [1, 2, 3]. The intensities of the diffraction peaks at 104 ($2\theta = 29.5^\circ$), 221 ($2\theta = 46^\circ$) and 110 ($2\theta = 25^\circ$) were considered to quantify the calcite, aragonite and vaterite, respectively. The quantization for a given sample can be carried out by comparison with standard samples with defined compositions. The XRD standard spectra were obtained [1] by measurements on calcite- vaterite and calcite-aragonite mixtures with different molar fractions (0 to 100%). They are named XC, XA and XV for calcite, aragonite and vaterite, respectively. For the calcite- aragonite mixture, the calibration equation was obtained by linear regression from the experimental data:

$$\frac{I_C^{104}}{I_A^{221}} = \frac{3,157 \times X_C}{X_A} \quad (1)$$

where I is the intensity of the peaks. A similar equation can be obtained for the mixture-calcite-vaterite:

$$\frac{I_C^{104}}{I_V^{110}} = \frac{7,691 \times X_C}{X_V} \quad (2)$$

Assuming that $X_C + X_A + X_V = 1$, the molar fractions in a sample can be determined from the following relationships:

$$\begin{aligned} X_A &= \frac{3,157 \times I_A^{221}}{I_C^{104} + 3,157 \times I_A^{221} + 7,691 \times I_V^{110}} \\ X_C &= \frac{I_C^{104} \times X_A}{3,157 \times I_A^{221}} \\ X_V &= 1 - X_A - X_C \end{aligned} \quad (3)$$

The presence of impurities does not affect the validity of these equations, provided that there is no chemical reaction between the impurity and the calcium carbonate or overlap

between the diffraction peaks used in equation 3 and those of the same impurity. These equations can be used to analyze the samples obtained with the solutions in the presence of humic substances.

References

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